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Mining and Beneficiation of Phosphate Ore

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Additional information is available at the end of the chapter

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Abstract

The first commercial production of phosphate rock began in England in 1847. A wide variety of techniques and equipment is used to mine and process phosphate rocks in order to beneficiate low-grade ores and remove impurities. The eighth chapter of this book deals with mining and beneficiation of phosphate ore. The principle and operating conditions of important parts of manufacturing process including separation, classification, removing of carbonates, calcination and flotation was described. The chapter ends with description of techniques used for extraction of rare earth element.

Keywords: Apatite, Phosphate Rock, Mining, Benefication, Separation, Calcination, Flotation, Extraction of Rare-Earth Element

Phosphate rock is an important mineral commodity used in the chemical industry and production of food. Phosphate ores show a wide diversity in the composition of their gangue materials but generally fall into one of the following categories based on major associated gangue materials [1],[2],[3],[4]:

1. **Siliceous ores:** these ores contain quartz, chalcedony or different forms of silica. Such ores could be upgraded economically by techniques such as flotation or gravity separation methods.
2. **Clayey ores:** contain mainly clays and hydrous iron and aluminum silicates or oxides as gangue materials. These impurities could be removed by simple beneficiation techniques such as scrubbing and washing. In some cases, dispersing agents would be necessary.
3. **Calcareous ores of sedimentary origin:** contain calcite and/or dolomite as the major impurities with small amounts of silica. It is usually difficult to remove the carbonate minerals efficiently from such ores by conventional techniques such as flotation or by physical separation methods. This is because the physical properties of carbonates and

phosphates are very similar. The separation by physical means becomes even impossible when the carbonate minerals are finely disseminated into the phosphate particles.

An alternative technique for the beneficiation of these ores is the calcination. Calcination is the process of heating the ore to a high temperature ranging from 800 to 1000°C to decompose CaCO_3 and MgCO_3 to CaO , MgO and gaseous CO_2 . The CaO and MgO formed are then removed as hydroxides by quenching the calcined product in water and washing. The most common chemical reagent used to enhance the removal of calcium and magnesium hydroxides is ammonium chloride.

Chemical dissolution of carbonate minerals (calcite and dolomite) from calcareous phosphate ores, without the calcination, using organic acids also proved to be capable of beneficiating the calcareous phosphate ores on the laboratory scale.

4. **Phosphate ores associated with organic matter (black or brown phosphates):** ores of this type are generally beneficiated by heating the ore up to about 800°C. This type of calcination burns organic material and residual organic carbon without significantly affecting the superior qualities of sedimentary phosphates such as the solubility and reactivity.

Furthermore, as a result of low calcination temperature, the reduction of calcium sulfate, present in ore, to corrosive calcium sulfide by the organic matter is minimized. During the burning of organic matter, the following two conditions must be kept: organic carbon must be decreased to less than 0.3% to minimize the gassing in the wet phosphoric acid processing, and apatite CO_2 must be maintained at a level close to 2% to allow good reactivity of calcined product.

5. **Phosphate ores containing more than one type of gangue minerals:** many sedimentary phosphate deposits contain mixtures of undesired constituents. These ores require a series of beneficiating operations during their processing depending on the type of gangue minerals present in each ore. This may include, after the size reduction, the combination of attrition scrubbing, desliming, flotation, gravity separation and/or calcination. Each flow sheet is to be designed after thorough characterization and testing of a representative sample of the exploited ore.

Igneous and metamorphic phosphate ores: the main gangue materials in these ores are sulfides, magnetite, carbonates (calcite, dolomite, siderite and ankerite), nepheline syenite, pyroxenite, foshkorite, etc. The processing of these ores may include, after crushing and grinding, washing, desliming, magnetic separation and flotation depending on the types of present gangue minerals. However, the flotation is a common step in all of them [1].

The quality factors of commercial phosphate rocks include [5]:

- i. **Physical factors**, which include the parameters such as the texture (hardness, porosity, cementing of coating phases), the particle size (coarse or cryptocrystalline), the degree of crystallinity of apatite and the effect of physical treatments (natural or calcined state).
- ii. **Chemical factors**, which include the parameters such as the content of phosphorus (BLP grade, **Section 9.3**), fluorine, carbonate and free carbonates in apatite. The

content of Fe and Al (expressed as $R_2O_3^1$), the content of Mg in phosphate and accessory minerals, the content of inert gangue mineral (insoluble oxides and silicates), the content of Na and K (phosphate and accessory minerals), organic matter (native and beneficiation reagents), chlorides (from evaporite salts), heavy metals (Cd, Pb, Zn, Hg), potentially toxic elements (Se, As, Cr, V) and radionuclides (U, Th, Ra, Rn).

Increasing world demand on fertilizer in the 1960s and 1970s and the need for phosphate feedstock stimulated the efforts to develop the techniques to beneficiate low-grade ores and remove impurities. It is highly desirable, for both economic and technical reasons, to remove as much of these impurities as possible, thus to increase the apatite content and the grade of phosphate feedstock and to improve the chemical quality. Phosphate ores can be beneficiated by many methods, and usually a combination of more methods is used [6],[7], [8].

The phosphate rock concentrate must meet the following conditions to be salable [4]:

- High P_2O_5 content (>30%);
- Low CaO/P_2O_5 ratio (<1.6);
- Low MgO content (<1%).

As will be mentioned in **Section 9.3**, the content of P_2O_5 is usually expressed as bone phosphate of lime. The treatment and utilization of phosphate ore is shown in **Fig. 1**.

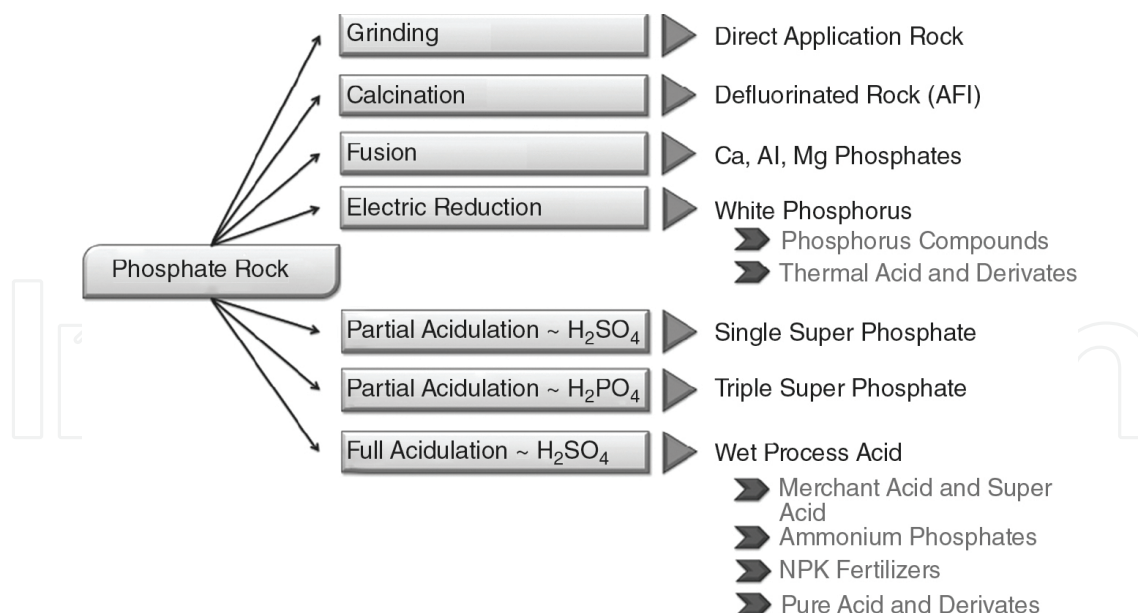


Fig. 1. The treatment of phosphate rock and end-product [8].

¹ Sesquioxides (R_2O_3) that consist of three atoms of oxygen and two atoms or radicals of other elements, e.g. Al_2O_3 , Fe_2O_3 and La_2O_3 .

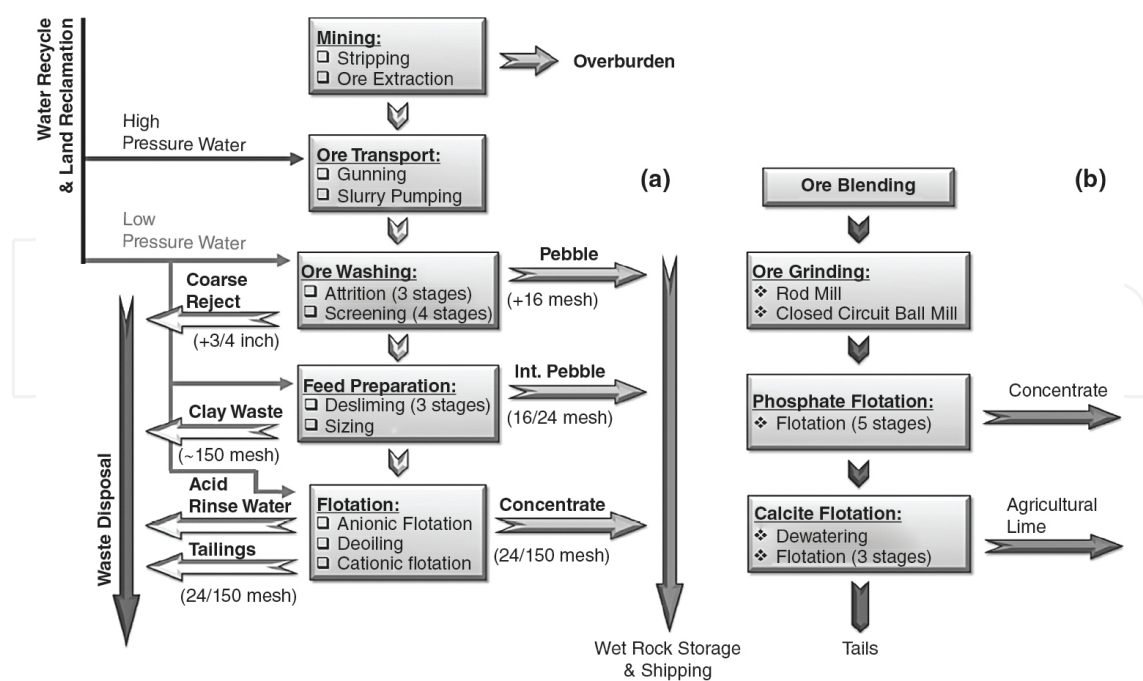


Fig. 2. Mining and beneficiation of sedimentary (a) and igneous (b) phosphate ore [8].

The example of a generic scheme for mining and beneficiation of sedimentary and igneous phosphate ore is shown in Fig. 2 [8].

8.1. Mining of phosphate ore

The first commercial production of phosphate rock began in England in 1847 and mining was undoubtedly by hand methods. Phosphate mining began in the United States in South Carolina in 1867. Platy phosphate rock beds were mined by hand and later by dredges; sorting was mainly by hand. Phosphate rock deposits were discovered in north and west Africa in the late 1800s. The exploitation of deposits in Algeria and Tunisia began prior to 1900. The production of phosphate rock began at many deposits in the north and west African region in the early to mid-20th century [5],[6],[9]. Currently, there are about 1635 operating world phosphate mines or occurrence worldwide [10].

A wide variety of techniques and many types of equipment are used to mine and process phosphate rock. The methods and the equipment used are very similar to methods and equipment used for coal mining. Phosphate rock is mined by both surface (open-cast, open-pit or strip mining) and underground methods. The surface mining can take many forms — from manual methods employing picks and shovels to highly mechanized operations. Surface mining is the most utilized method by far for mining phosphate deposits. In high-volume applications, the surface mining methods are typically less costly and are generally the preferred methods when the deposit geometry and other factors are favorable [5],[6],[11].

Open-cast mining has developed into a versatile method with plenty of variations to match the mining depth, the slope of the original topography and the types of equipment available. The two major variations of open-cast mining are [12]:

1. **Area mining**, which is carried out on relatively flat terrain with flat-lying seams. Mining cuts are made in straight, parallel panels, running across the property.
2. **Contour mining** is conducted in hilly or mountains terrain, with cuts placed on the contours of the topography.
3. **Other** variations of the open-cast mining, including the box-cut and block-cut mining, are often utilized as well.

The open-cast mining cycle consist mainly of [11],[12]:

- i. **Cleaning**: rotary brush of dozer cleans the top of the seam;
- ii. **Drilling**: small auger or percussion drill used where needed;
- iii. **Blasting**: ANFO or alternatively ripping with dozer;
- iv. **Excavation**: front-end loader, power shovel, continuous miner (designed for surface mines);
- v. **Haulage**: truck, tractor-trailer, belt conveyor, hydraulic conveyor, rail;
- vi. **Auxiliary operations**: reclamation, slope stability, haul road construction and maintenance, equipment maintenance, drainage and pumping, communications, power distribution, dust control and safety.

Because the profile of the deposit layer is different, the mining process selection is needed to be adapted in order to reach the best economic effect [11]:

The open-cast mining has numerous advantages and disadvantages as well. The main advantages are [12]:

- a. Higher productivity, efficiency and safety than for underground mining;
- b. The utilization of large equipment reduces the unit cost;
- c. Modest development requirements allow rapid exploitation;
- d. Relatively flexible, can increase the production by expanding operations.

The disadvantages of open-cast mining process are:

- a. The economic limits of the method and the technological limit of the equipment impose the depth limit, which is generally about 90 m;
- b. The economics imposes the limits of stripping ratios;
- c. Extensive environmental reclamation of the surface is required.

8.2. Separation and classification

Separation and classification² are very important elemental manufacturing processes in many industries such as the mining and chemical industries. The equipment using many different methods of separation is applied in these processes [13],[14]. Used concentrating devices depend on the fluid, the force field and the specific properties of particles, such as the density, size, shape, chemistry, surface chemistry, magnetism, conductivity, color and porosity. Various concentrating devices are applicable to particles according to their size ranges (Fig. 3), and for any given size range, several processes or devices might be used. The gravity concentration works the best in the range from 130 mm to 74 μm [15].

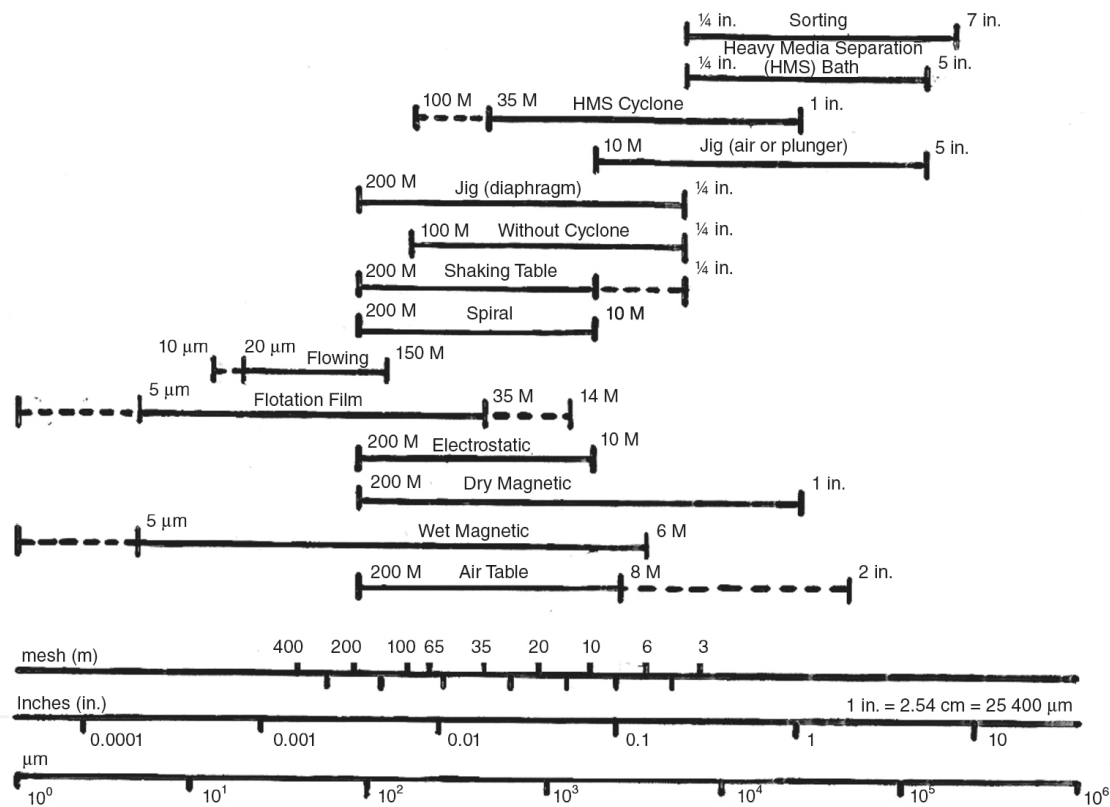


Fig. 3. Approximate range of applicability of various concentrating devices (M = mesh, Tyler standard) [15].

In phosphate rock beneficiation, the availability of water is of primary importance and may determine the process or processes used. Fine-grained impurities can often be removed from phosphate ores by using the combinations of comminution, scrubbing, water washing, screening and/or hydrocyclones. The disposal of tiny ore constituents (slimes) can be problematic. The beneficiation technique of froth flotation (described in Section 8.7) is widely used within the world phosphate rock industry [4],[6].

² Classification is defined as the separation of a mixture of solid particles into various fractions according to their sizes or densities [14].

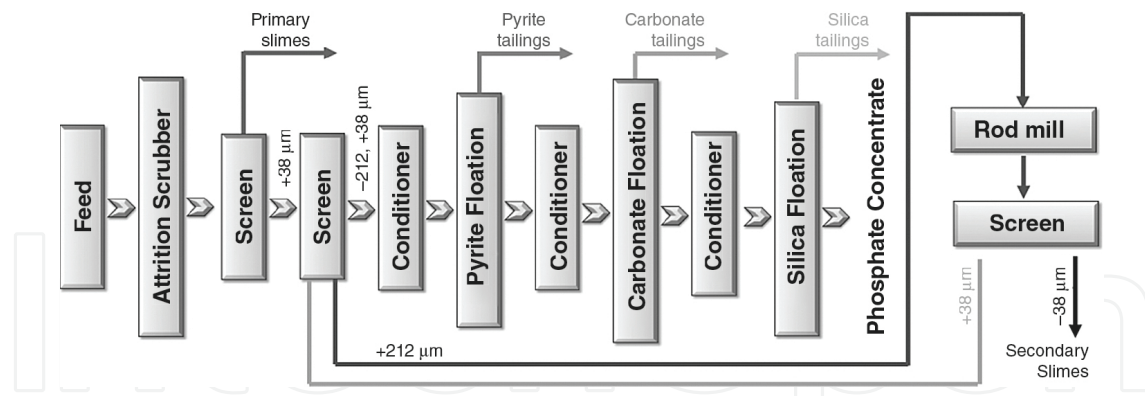


Fig. 4. Beneficiation of phosphate rock containing carbonates, silica and pyrite as the main gangue materials [1],[7].

Ore type	Beneficiation method		
	Flotation	Calcination	Organic acid leaching
Igneous	The best approach	Not applicable	Not applicable
Sedimentary with siliceous gangue	The best approach	Not applicable	Not applicable
Sedimentary with calcareous gangue	Advantages —	Advantages Low water consumption. Complete elimination of the carbonate gangue.	Advantages Very selective. Acid plants have low capital cost. Method has few environmental hazards. Leaching does not affect phosphate minerals. Organic acid can be recycled. Water consumption equal to convectional beneficiation. Final product has good quality and purity. Organic acid salts are soluble in water and easily filtered from solid product.
	Disadvantages Method has not given satisfactory results. Not applicable in many cases.	Disadvantages Calcination. Plants high capital cost. Needs high thermal energy. Calcined product has no desirable quality. Calcination decreases the product solubility. Process is time consuming.	Disadvantages Economic aspects are not well established. Organic acid price is high.

Table 1. The comparison of phosphate ore beneficiation methods [16].

Effective beneficiation can be achieved by various processes depending on the liberation size of phosphate and gangue minerals and other ore specifications. Different processes like screening, scrubbing, heavy media separation, washing, roasting, calcinations, leaching and flotation may be used. For example, crushing and screening are used to remove coarse hard siliceous material, and attrition scrubbing and desliming are used to remove clayey fine fractions. If silica is the main gangue material, flotation is the conventional mineral processing technique used. Igneous-type ores are also amenable to flotation, which is the best approach for the processing of this type of phosphate ore [16].

8.3. Electrostatic separation

Almost all minerals show some degree of conductivity. The electronic separation process uses the difference in electrical conductivity or surface charge of the mineral species of interest. The electrostatic separation process is generally confined to recovering valuable heavy minerals from beach-sand deposits. However, the growing interest in plastic and meta recycling has opened up new applications in secondary materials recovery [15].

When particles come under the influence of electrical field, depending on their conductivity, they accumulate charge that depends directly on the maximum achievable charge density on the particle surface. These charged particles can be separated by differential attraction or repulsion. Therefore, the first important step in electrostatic separation is to impose an electrostatic charge onto particles. Three main types of charging mechanism are the contact electrification or triboelectrification, the conductive induction and the ion bombardment (Fig. 5). Once the particles are charged, the separation can be achieved by the equipment with various electrode configurations [13],[15].

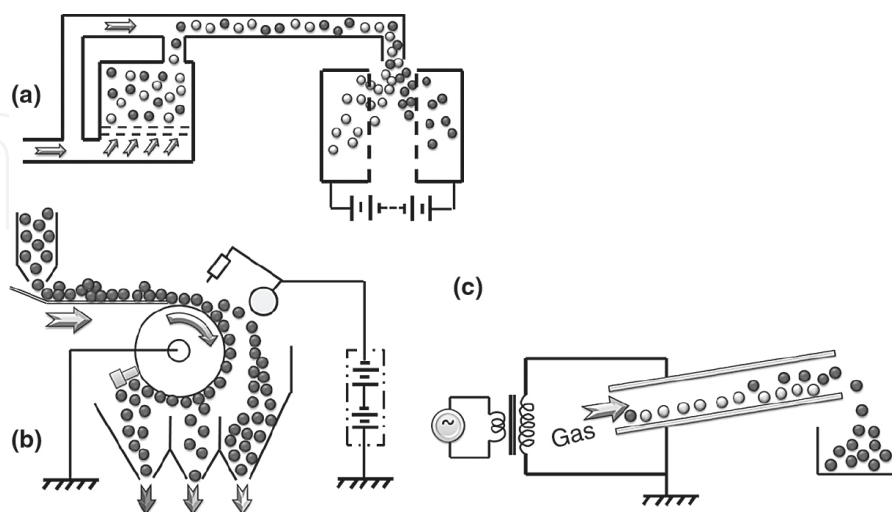


Fig. 5. Representative methods of electrostatic separation: contact charge (a), ion attachment (b) and induced charge (c) [13].

In the combination with attrition, desliming and gravity separation, the electrostatic separation technique is successful in the beneficiation of phosphate ores by removing silica and/or carbonates, mostly on laboratory scale. However, low capacity of electrostatic separators limits their use in large-scale production. This technique is used to concentrate the phosphate ores of different types [1].

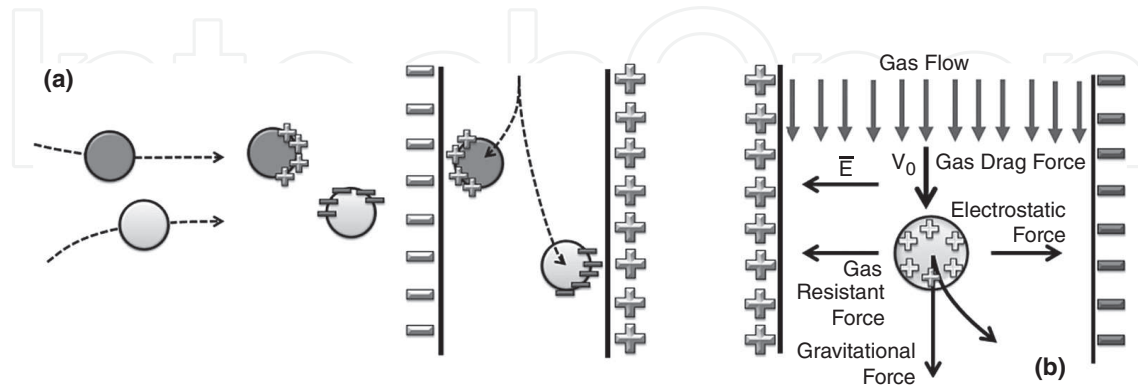


Fig. 6. Particle charging mechanism: the particle charged positively has lower work function and the particle charged negatively has higher work function (a) [1] and the illustration of the separator chamber (b) [17].

The triboelectrification is a type of electrostatic separation in which two nonconductive mineral species acquire opposite charges by contact with each other. The particle charging process is the critical step for the triboelectrostatic separation since the separation efficiency is a function of the difference in charge polarity and the magnitude of different particles.³ Oppositely charged particles can be separated under the influence of electric fields. This process uses the difference in the electronic surface structure of the particles involved. A good example is the strong negative surface charge the silica acquires when it touches carbonates and phosphates. The surface phenomenon that comes into play is the work function, which may be defined as the energy required to remove electrons from any surface (**Fig. 6(a)**). The work function is defined as the minimum energy that must be supplied to extract an electron from a solid. The particle that is charged positively after particle-particle charging has lower work function than the particle that is charged negatively [15],[17].

The particle residence time, i.e. the time for the particle traveling through the separation chamber (**Fig. 6(b)**), is controlled by the particle vertical motion. However, the horizontal particle motion (y) is controlled by electric field deflection. The relation governing the horizontal displacement (x) of moving particle is [17]:

$$\frac{d^2\bar{x}}{dt^2} = \bar{E} \frac{q}{m} \quad (1)$$

³ The charge density achieved with conventional pneumatic chargers (including tubing charger, cyclone, honeycomb, static mixer, etc.) and belt charger is about $5 - 8 \cdot 10^{-6} \text{ C/m}^2$. Since the theoretical limit for the charge is $2.63 \cdot 10^{-5} \text{ C/m}^2$, clearly, there is a huge potential in improving the charging efficiency [17].

where m is the mass of particle, x is the horizontal displacement vector, t is the time, E is the electric field intensity and q is the charge of particle. The charge-to-mass ratio q/m is referred to as the particle specific charge. If the resistance of air with the viscosity η is also considered, the horizontal motion of moving spherical particle of radius r is given by the equation:

$$\frac{d^2\bar{x}}{dt^2} + 6\pi \frac{\eta}{m} r \frac{d\bar{x}}{dt} = \bar{E} \frac{q}{m} \quad (2)$$

From Eq. 2, the speed of the particle as a function of time can be derived:

$$\frac{d\bar{x}}{dt} = \bar{E} \frac{q}{6\pi\eta r} \left[1 - \exp\left(-\frac{t}{m / 6\pi\eta r}\right) \right] \quad (3)$$

where $t \gg \frac{m}{6\pi\eta r}$ or $t \rightarrow \infty$. The terminal horizontal speed of particle is:

$$\left(\frac{d\bar{x}}{dt} \right)_{horizontal} = \bar{E} \frac{q}{6\pi\eta r} \quad (4)$$

Under these conditions, the terminal horizontal speed is independent of the mass. However, since the time t is in the range of milliseconds, the mass does play an important role in determining the horizontal motion of the particle as well as the resultant trajectory that affects the separation performance [17].

The particle motion in the vertical direction is influenced by the gravitational force and gas drag force. The governing equation is [17]:

$$\frac{d^2y}{dt^2} = 6\pi r \frac{\eta}{m} \frac{dy}{dt} + g \quad (5)$$

where η is the dynamic viscosity of gas and g is the gravitational acceleration. For the initial conditions of $t = 0$, $y(0) = 0$ and $dy(0)/dt = V_0$, Eq. 5 can be solved as follows:

$$y(t) = \frac{(g + V_0 E) \exp(Bt) - Bgt - g - V_0 B}{B^2} \quad (6)$$

where $B = 6\pi\eta r/m$. The particle trajectories can be obtained from Eqs. 4 and 6.

The tube-type separator has the pre-charging zone and the separation zone as the integral parts of the machine (Fig. 7(a)). The pre-charging zone, or the triboelectrification process, exploits the difference in the electronic appearance of the particles involved. The particles become

charged by the particle-particle contact, particle-wall contact or both. The particle-particle contact between different particles results in the transfer of electrons (charges) from the surface of one particle to the surface of the other one. After this transfer, one of the particles is positively charged and the other one possesses the negative charge. The separation zone consists of two vertical walls of rotating tubes, which oppose each other and which are electrified by opposite potential. As the charged particles enter the separation zone, they become attracted by oppositely charged electrodes. The separated products are collected at the base of separator. This separator removes very effectively silica from other nonconductive minerals, such as calcium carbonate, phosphate and talc [15].

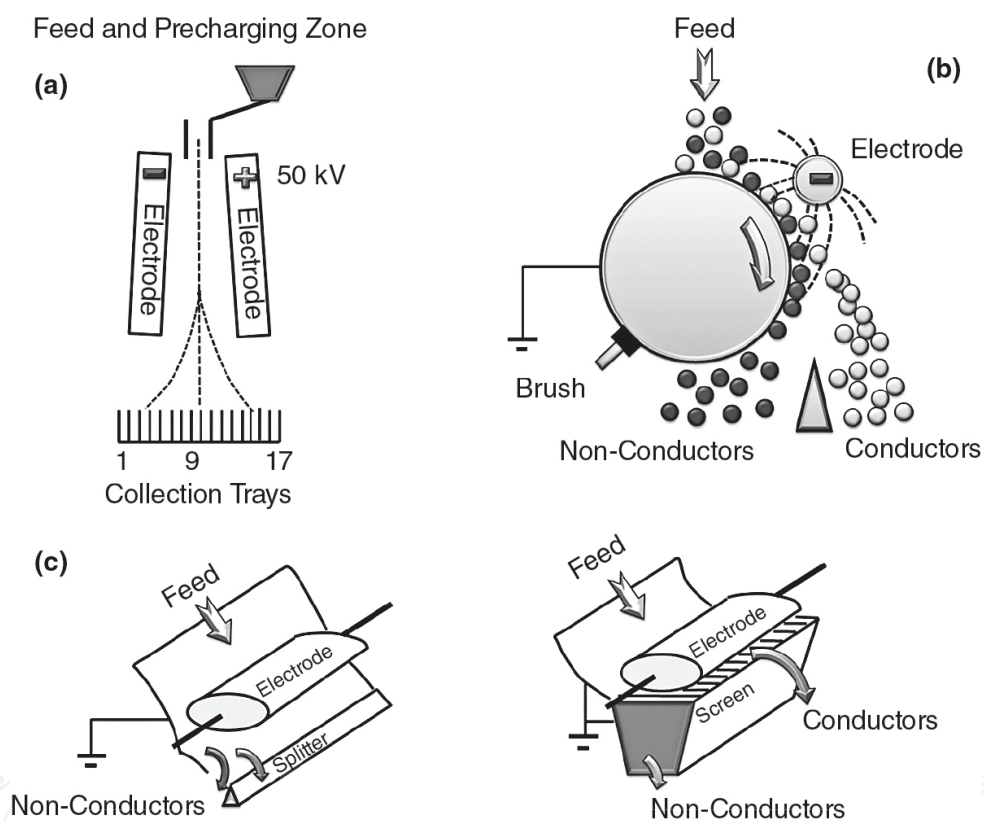


Fig. 7. Operating principle of electrostatic separator: (a) V-stat separator, (b) plate-type separator and (c) roll-type separator [15].

In the horizontal belt-type separator, fast-moving belts travel in opposite directions adjacent to suitably placed plate electrodes of the opposite polarity. The material is fed into a narrow gap between two parallel electrodes. The particles are swept upward by a moving open-mesh belt and conveyed in opposite directions, thus facilitating the particles' charging by contact with other particles. The electric field attracts the particles up or down depending on their charge. The moving belts transport the particles adjacent to each electrode towards opposite ends of the separator [15].

8.4. Magnetic separation

In 1792, a patent was filed by WILLIAM FULLARTON describing the separation of iron minerals with a magnet.⁴ The early applications were based on the intrinsic magnetic properties of sediments for the separation. In 1852, magnetite was separated from apatite by a New York company on a conveyor belt separator. Later, a new line of separators was introduced for the separation of iron from brass fillings, turnings, of metallic iron from furnace products and of magnetite from plain gangue. The 1950s were the time of great expansion in the field of magnetic separations as the introduction of high-gradient magnetic separation (HGMS) systems permitted faster and more general magnetic separation processes. More recently, the separations using external magnetic fields have become common processes in biotechnology, where they are used for both protein purification as well as flow cytometry [18],[19].

Electromagnets almost completely replaced permanent magnets as the field-generating elements in drum separators [20]. Recent progress in magnet technology has realized economically and operationally favorable cryocooler-cooled⁵ [21] superconducting magnets, which can be used for commercial applications [22]. The first large superconducting⁶ [23] separator has been operating successfully in the USA since May 1986 and a larger system was installed with twice the capacity in 1989. A revolutionary design for the superconducting magnetic separator with a reciprocating canister system was installed and successfully operated for clay processing in May 1989. Following this, a number of other reciprocators have been installed for kaolin processing in the places as far apart as Brazil and Germany [24].

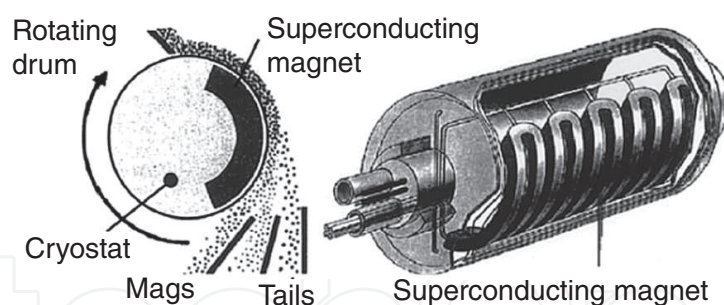


Fig. 8. Drum separator using a multi-pole superconducting magnet (Klochner Humbolt-Deutz Cologne, Germany) [22].

⁴ The properties of magnetic materials were identified as early as 6th century BC, but the means by which magnets could move material remained only a curious phenomenon until the late 18th century. The background for electricity and magnetism, the reasons that magnets could move materials, were explained by GAUSS AND HELMHOLTZ [18].

⁵ All superconducting devices share the need for sufficient refrigeration to overcome their low-temperature heat loading. This loading comes typically in two forms: (1) heat leaks from the surrounding and (2) internal heat generation in the device. In addition, the refrigeration system needs to bring the superconducting device from ambient temperature to its low operating temperature in reasonable length of time [21].

⁶ After Kamerlingh Onnes's pioneering the demonstration in 1908 that the last so-called permanent gas helium could indeed be liquefied. His follow-up discovery of superconductivity in 1911 introduced the zero electrical current resistivity to the world. It was theorized that one could go beyond the resistive limit of a copper wire to develop a superconductor that could carry any amount of current but without the ohmic loss [23].

Despite all this progress, the majority of the commercial magnetic separators fulfill only the simple technological objective of the removal of magnetic substances without the ability to classify them. Only three classical separation products (tails, middlings and mags, **Fig. 9**) are usually obtained [25].

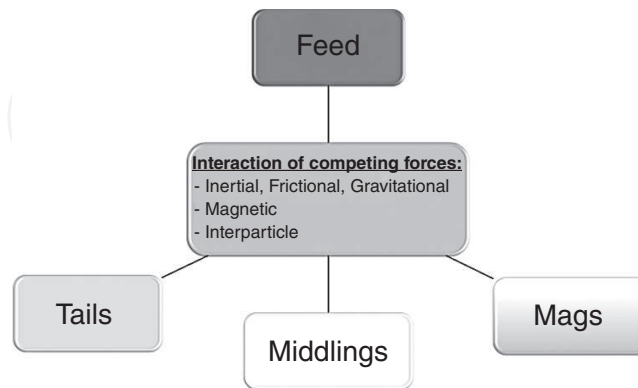


Fig. 9. Classical magnetic separation products [25].

Unlike the conventional filtration methods that use the blocking-type filtration, the secondary waste is not produced in high-gradient magnetic separation (HGMS), which is also known as the magnetic or electromagnetic filtration. Furthermore, because HGMS systems use much higher magnetic forces than conventional magnetic separation techniques, it can also be used to separate rapidly large quantities of diluted suspension [22].

According to the applied separation method, two classes of magnetic separators are recognized [26]:

- i. Separators that deflect the magnetic particles from the main stream, e.g. open-gradient magnetic separation (OGMS);
- ii. Separators that usually collect the magnetic particles in matrices, e.g. high-gradient magnetic separation (HGMS).

Although current separators usually achieve high grades of separation, they cannot classify the particles⁷ as they are being separated. The magnetic separator in which these two steps are performed at the same time and in the same machine was proposed by AUGUSTO and MARTINS [26].

Magnetic separation has been considered for many years a valuable method to achieve the purification of streams of particles (dry or wet) [26]. Magnetic separators have unrestricted industrial applications and are widely used in mineral beneficiation, food, textiles, plastic and ceramic processing industries. The separation efficiency of magnetic separator depends on the

⁷ Differential magnetic classification and the selectivity are different definitions. The selectivity is defined as the ability to separate one certain kind of magnetic particles from all others, independently of how close their magnetic susceptibilities may be [25].

material characteristics and the design features of equipment along with the optimization of process variables [27].

The magnetic force (\vec{F}_m) acting on weakly magnetic particle flowing in a fluid is given by the equation [19]:

$$\vec{F}_m = \frac{1}{\mu_0} (\kappa_p - \kappa_f) V_p B \nabla B \quad (7)$$

where B is the magnitude of magnetic flux density at the particle position, μ_0 is the magnetic permeability of vacuum, κ_p is the volume susceptibility of the fluid and V_p is the volume of the particle. The magnetic force on a particle is then proportional to the magnitude of magnetic flux density and the gradient. The magnetic field can be increased using a stronger magnet having more ampere turns, and the field gradient can be increased by changing the magnetic polarities and using a steel wool matrix. For sufficiently strong magnetic particles such as iron, magnetite and maghemite, it is advantageous, and **Eq. 7** can be written as:

$$\vec{F}_m = \mu_0 V_p M \nabla H \quad (8)$$

where M is the magnetization of the particle and H is the magnitude of magnetic field intensity at the particle position [19].

The basic principle behind magnetic separations is remarkably simple and remains unchanged from these early examples. It is based on a simple fact that materials with differing magnetic moments experience different forces in the presence of magnetic field gradients; thus, externally applied field can hand pick the components with distinctive magnetic characteristics out of physically similar mixtures [18]. When one of the major gangue constituents is magnetic, magnetic separators are used as one of the steps in the flow sheet to remove the magnetic constituents. This is mostly used in the beneficiation of igneous phosphate rocks. However, it was also used for the beneficiation of some sedimentary phosphate ores [1].

Paramagnetic minerals have higher magnetic permeability than the surrounding medium, usually air or water, and they concentrate the lines of source of an external magnetic field. The higher the magnetic susceptibility, the higher the field intensity in the particle and the greater the attraction up the field gradient toward increasing field strength. Diamagnetic minerals, on the other hand, have lower magnetic permeability than the surrounding medium and they repel the lines of force of magnetic field. These characteristics cause the expulsion of diamagnetic minerals down the gradient of the field towards decreasing field strength. This negative diamagnetic effect is usually orders of magnitude smaller than the positive paramagnetic attraction. Thus, a magnetic circuit can be designed to produce higher field intensity or higher field gradient or both to achieve the effective separation [15].

Magnets are used in the mineral industry to remove the tramp iron that might damage the equipment and to separate minerals according to their magnetic susceptibility. According to the intensity of the magnetic field, two types of magnetic separators are recognized [15]:

- a. **Low-intensity magnetic separators** have the flux densities up to 2000 G⁸ [28]. These separators are mainly used to remove the ferromagnetic material, such as iron, to protect downstream unit operations, such as conveyor belts, or to scalp ferromagnetic materials to improve the performance for permanent or electromagnetic separators used to separate weakly magnetic materials. Low-intensity separators can treat wet slurry or dry solids.
- b. **High-intensity magnetic separators** separating paramagnetic or weakly magnetic particles require higher flux density. This higher density is achieved by designing the electromagnetic circuitry that can generate the magnetic force of up to 2 tesla. For example, in a silica sand processing plant, these separators are used to remove weakly magnetic iron-bearing particles.

Rotating-drum magnetic separators (**Fig. 10**) are mainly used in mines. The rotating disc magnetic separator is used in so-called ferritic processes [22].

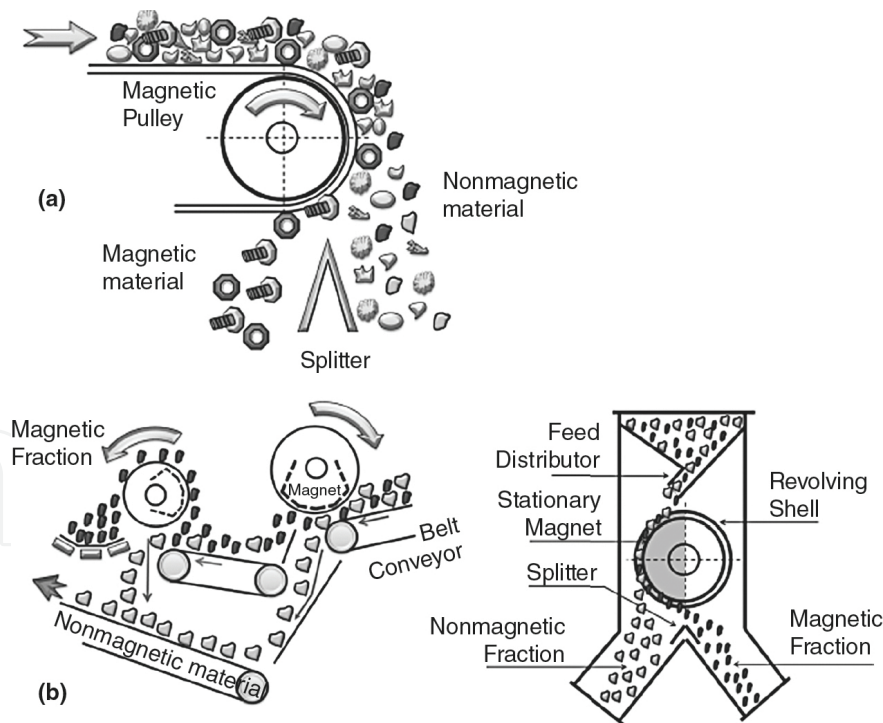


Fig. 10. Typical magnetic pulley (a) and magnetic drum operating as lifting magnet (b) [15].

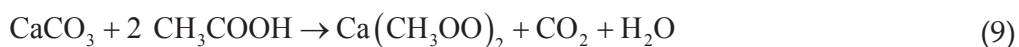
⁸ The gauss (G or Gs) is a unit of magnetic field (magnetic flux density) named after CARL FRIEDRICH GAUSS ($1 \text{ G} = 10^{-4} \text{ T} = 1 \text{ cm}^{-1/2} \text{g}^{1/2} \text{s}^{-1}$) [28].

8.5. Removing of carbonates

The removal of carbonates from phosphate rock has been the focus of significant research efforts. Several countries have large deposits of phosphate rock that contain significant amounts of calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). The calcination of phosphate ores to remove carbonates is expensive because of high costs of energy. Calcination is practiced commercially at several phosphate rock mining operations around the world, mainly to improve final product quality by removing minor amounts of carbonates and organic matter. Calcination is also used to remove carbonates where the cost of natural gas is very low [1],[6].

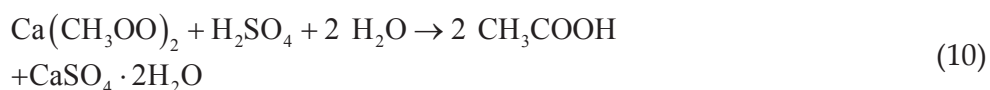
Calcium and magnesium carbonates are readily dissolvable in both mineral (strong acids) and organic acids (weak acids). In the case of calcareous phosphate ores, although mineral acids dissolve carbonates at high reaction rates, they also attack the phosphorus-bearing minerals and cause losses in the P_2O_5 content of the ore; hence, they are not appropriate if the intention is only to beneficiate the ore not to dissolve phosphates. To avoid this problem, organic acids were studied as carbonate leaching agents, although their reaction rates are low. These organic acids may be expensive and will certainly add to the production cost. On the other hand, they are selective to leaching carbonates, their capital cost is low, they do not cause environmental hazards and they can be recycled [1].

The organic acids most commonly used in carbonate leaching are acetic acid, citric acid and formic acid. They are used for some specific advantages (may be the cost, availability, etc.). Suggested reaction between acetic acid and carbonates is [1],[16],[29]:



The dissolution kinetics of calcareous material with acetic acid solution was found to fit the shrinking core model for the reaction-controlled process. The activation energy was determined to be $41.0 \text{ kJ} \cdot \text{mol}^{-1}$, which is consistent with a chemically controlled reaction. The process is driven by the surface chemical reaction kinetic model: $(1 - (1 - \alpha)^{1/3})$ [30].

Acetic acid may be recovered by reversing the above reaction at high CO_2 pressure in a separate reactor or by using sulfuric acid to precipitate calcium sulfate and to liberate acetic acid:



It is noted that the by-products such as calcium sulfate (gypsum) could be used and/or sold to lower the costs of acetic acid and its recovery by sulfuric acid (Eq. 10). Similarly, formic and lactic acids (Eq. 11) can be used to dissolve carbonate minerals [16],[30]:

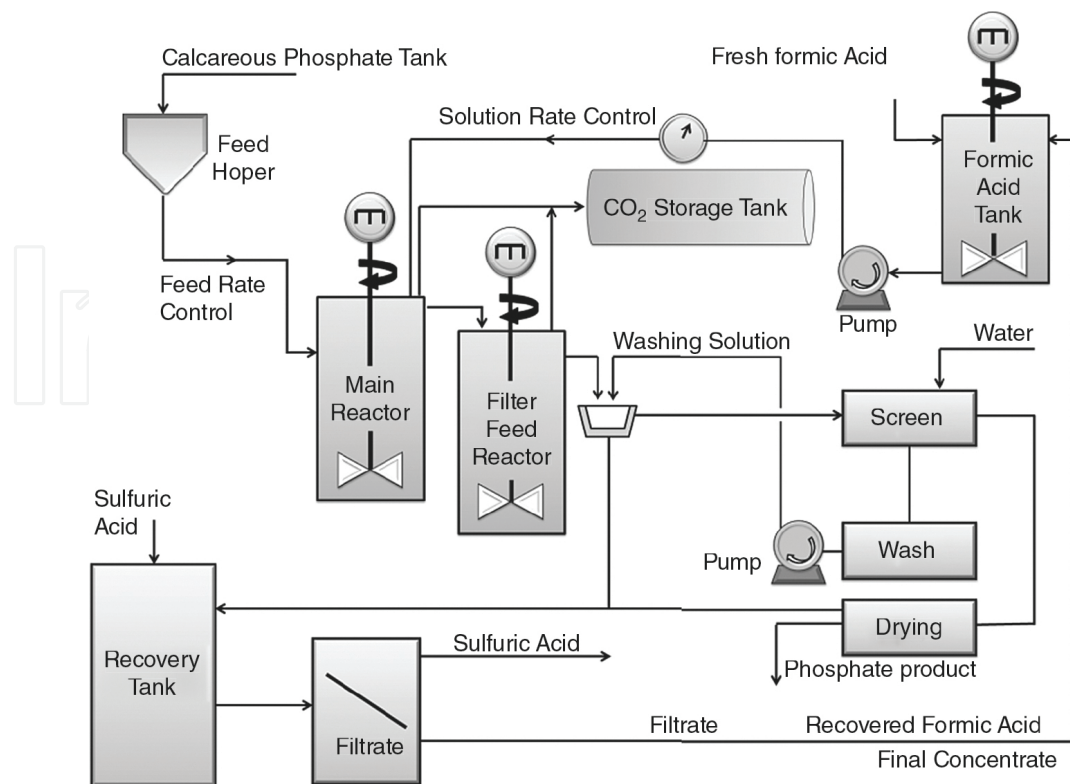
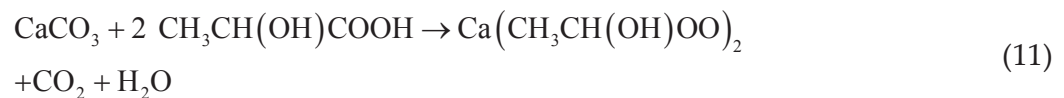


Fig. 11. Proposed flow sheet for leaching of phosphate rock/ores using formic acid [16].



The main factors investigated by the researchers were: leaching reagent, acid concentration, reaction time, liquid/solid ratio (pulp solid percent), temperature, particle size distribution, stirring speed and type and nature of ore [16].

8.6. Calcination

More than 10% of the world's marketable phosphates are produced by calcination. Traditionally, the heat treatment of phosphate ores is defined as heating up the ore to a certain temperature to obtain a product with specific properties. The main processes that take place during the thermal treatment of apatite ore are [1],[3],[31],[32]:

1. **Drying**, i.e. the evaporation of water within the temperature range from 120 to 150°C;
2. **Pyrolysis of organic matter** within the temperature range from 650 to 750°C is important for black or brown phosphates;

3. **Thermal decomposition of carbonates**, i.e. the calcination within the temperature range from 850 to 1000°C;
4. **Removal of fluorine**, i.e. the **defluorination** at temperatures higher than 1350°C.

The calcination process of phosphate ore is schematically shown in **Fig. 12**.

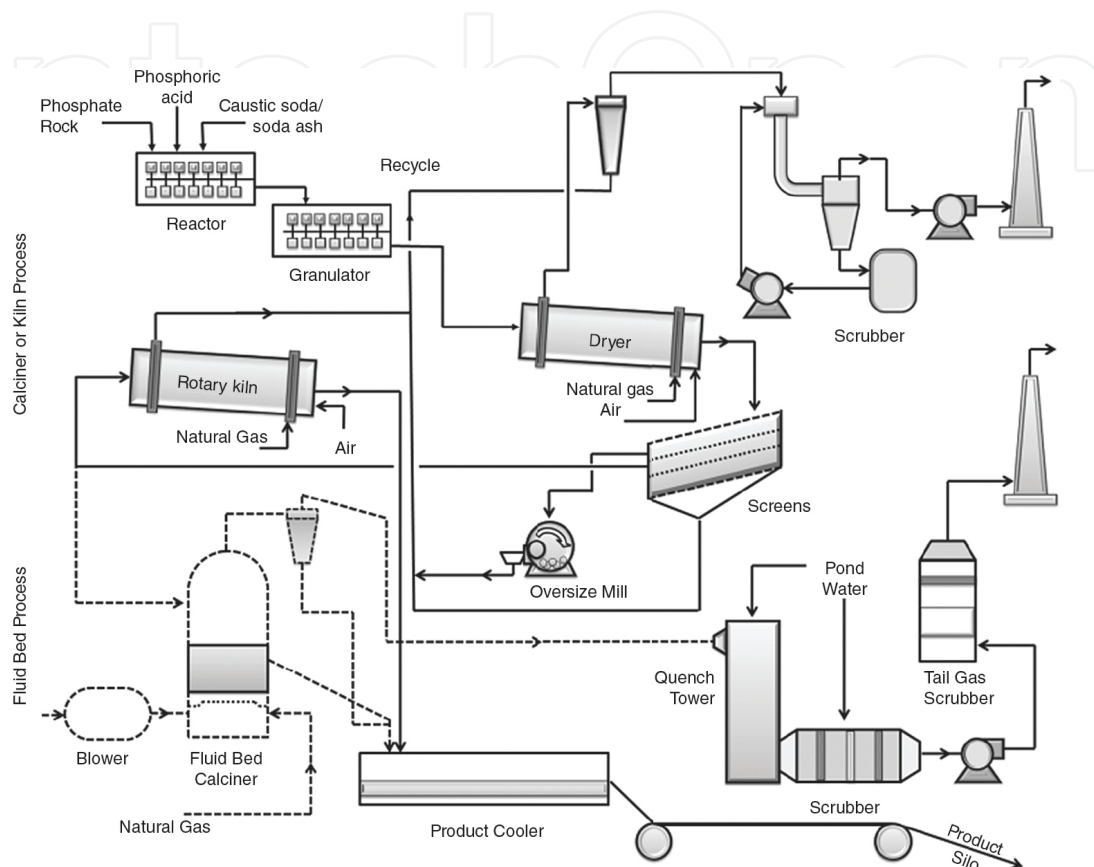


Fig. 12. Illustration of the defluorination process of phosphate rocks [1].

There are various types of units that can be used for the calcination of phosphate ores, such as [1]:

- i. **Vertical-shaft kilns** [33],[34]: are the most popular type of kilns, having varying heights, diameters and constructional details. There are two types, namely mixed- (a) and unmixed-fuel type (b). The construction of a vertical shaft may be cylindrical, conical or a combination of both shapes with varying diameters in different zones (**Fig. 13(a)**).
- ii. **Fluidized-bed reactors (calciners)** [33],[34]: the hot gases perform two functions: (1) fluidize the particles and (2) transfer the heat to the particles (**Fig. 13(b)**). Since the fluidization is a function of particle size, only fine particles can be introduced as the feed particles.

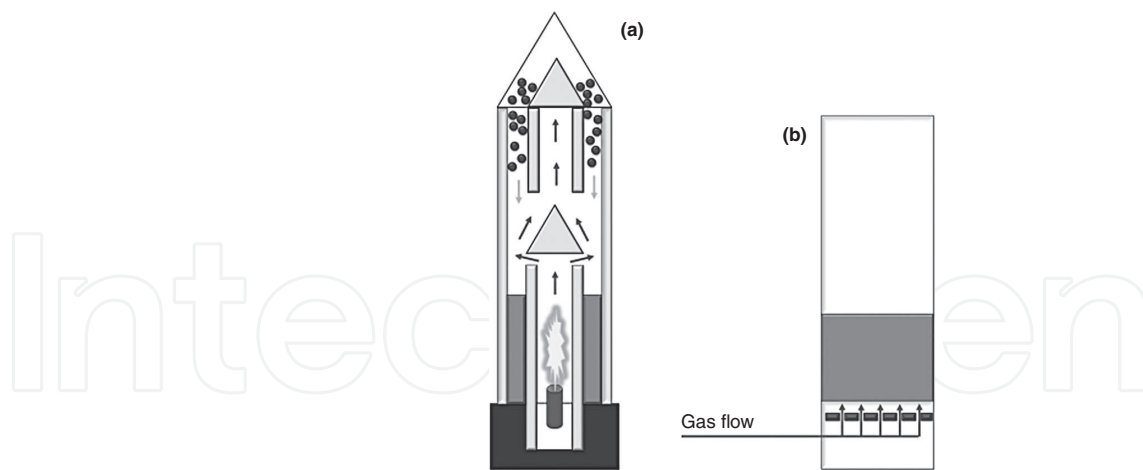


Fig. 13. Schematic diagram of annular-shaft kiln (a) and fluidized-bed calciner (b) [34].

- iii. **Rotary kilns**⁹ [33],[34],[35]: are extremely versatile incineration systems. They differ greatly in size with respect to their diameter (150 – 390 cm) and length (1800 – 1350 cm). Basic rotary kiln is composed of a cylindrical, refractory-lined steel shell, supported on two or more trunnions. The kiln is gently sloped (usually up to 0.03 m/m) and rotates slowly (1 – 5 rpm, the rotation rate is usually less than 2 rpm). The kiln may be operated in the co-current (parallel) or countercurrent mode (Fig. 14) with respect to the relative direction of gas and solid flow.

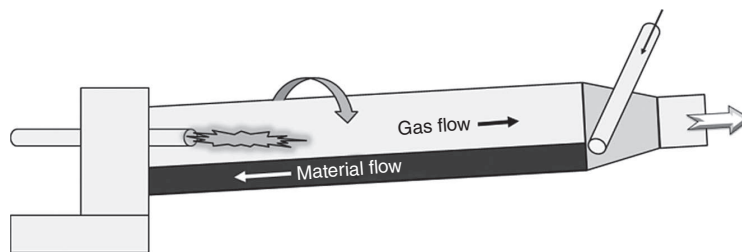


Fig. 14. Schematic representation of countercurrent flow rotary kiln [34].

The rate of movement of the material through the kiln may be estimated using several relationships, e.g.:

$$\Theta = \frac{0.19 L_T}{NDS} \quad (12)$$

where Θ is the residence time [min], L_T is the length of the kiln [m], N is the kiln rotation velocity (rpm), D is the kiln internal diameter [m] and S is the slope of the

⁹ Rotary kilns are synonymous with cement and lime kilns probably because of the history of their evolution and development.

kiln [m/m]. Since the rotary kiln is divided to zones, the relationships should, more appropriately, be used for several reasonably uniform zones along the kiln and the total residence time can be calculated as the sum of the residence times for the individual zones.

- iv. **Traveling grate-kilns, rotary kilns systems** [36],[37]: use low strength, somewhat wet pellets. These pellets are placed in a uniform bed upon a traveling grate, hot air being blown upward from below. The dehydration and partial calcination occur on the grate. Pellets are then fed to a short rotary kiln. The example of grate-kiln technology for the thermal treatment of pellets is shown in **Fig. 15**. The main advantages of this system are controlled feed rate, no flushing of materials into the kiln, no segregation of raw material due to different shapes and densities, avoidance of fluidization of the material bed, minimal dusting, etc.

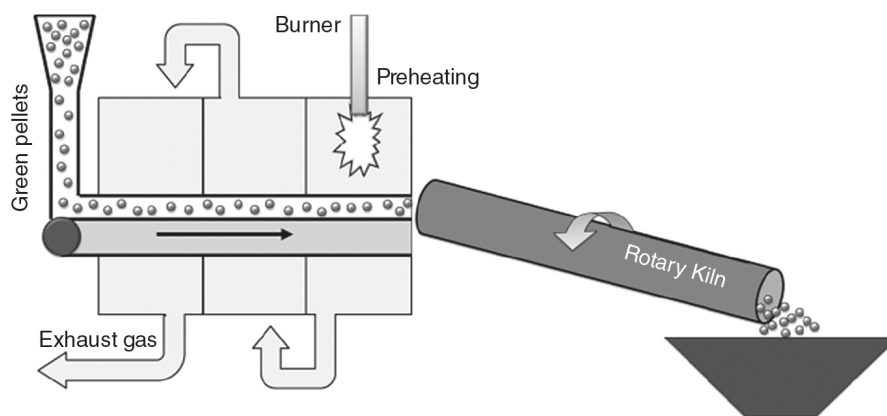


Fig. 15. Thermal treatment of pellet using grate-kiln technology [36].

- v. **Flash calciner** [31],[38],[39]: is one of more recent developments in calcination, but it is not really a kiln. There are three main elements including preheater (1), flash calciner (2, **Fig. 16**) and cooler (3).

The unique characteristics of flash calcination are particularly suited to pressing phosphate. Phosphate is a complicated mineral that varies from deposit to deposit with each ore requiring its own special processing consideration. During thermal treatment, it is important not to destroy the delicate crystal structure of phosphate by overheating. Flash calcination rates, very good oxygen contact and rapid cooling, all of these characteristics, are very important in the production of high-quality calcined phosphate. The operating conditions in the range from 800°C to 1000°C are required.

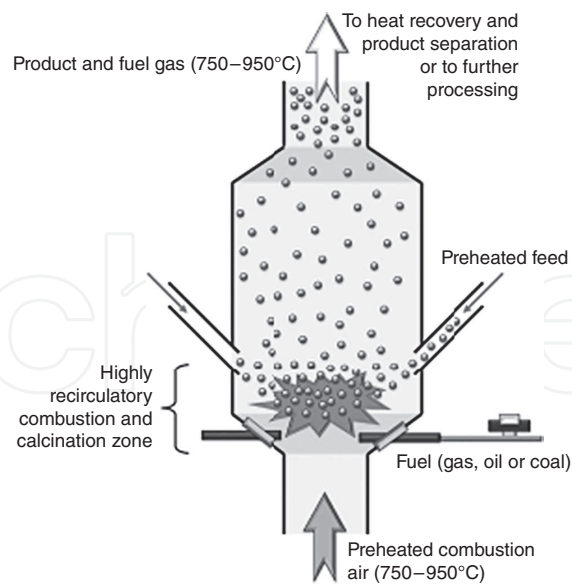


Fig. 16. Schematic representation of flash furnace [38].

8.7. Flotation

Flotation is a selective separation process that consists of attaching hydrophobic particles to rising air bubbles to form a particle-rich froth on the suspension surface, which flows over the lip of the cell. Hydrophilic particles do not attach to the bubbles and settle at the bottom to be discharged. Flotation has been the workhorse of mineral industry for over 100 years and has been expanded into many other areas, including deinking of wastepaper for recycling, water treatment and separation of plastics, crude oils, effluents, microorganisms and proteins [40].

The beneficiation of phosphate ores using froth flotation method has been practiced for at least 65 years. Extensive research work has been carried out in the last 25 years on various phosphate-containing ores. Despite extensive research and industrial experience, there are some challenges remaining in particular in beneficiation of siliceous-, calcite- and heavy mineral-containing phosphate ores [41].

Despite the fact that the flotation of apatite is difficult due to its physicochemical properties being similar to other minerals present in phosphate ores [42],[43], the froth flotation is widely used in mineral processing technologies to separate finely ground valuable minerals from a mixture with gangue minerals initially present in a pulp. The technique involves the contact of air bubbles with the solids [44]. Flotation technology is also used to remove suspended impurities during the treatment of wastewater, water purification, recovery of bacteria, cereal cleaning, recovery of metal and colloidal matters and recovery of ions and surfactants from the solution [45].

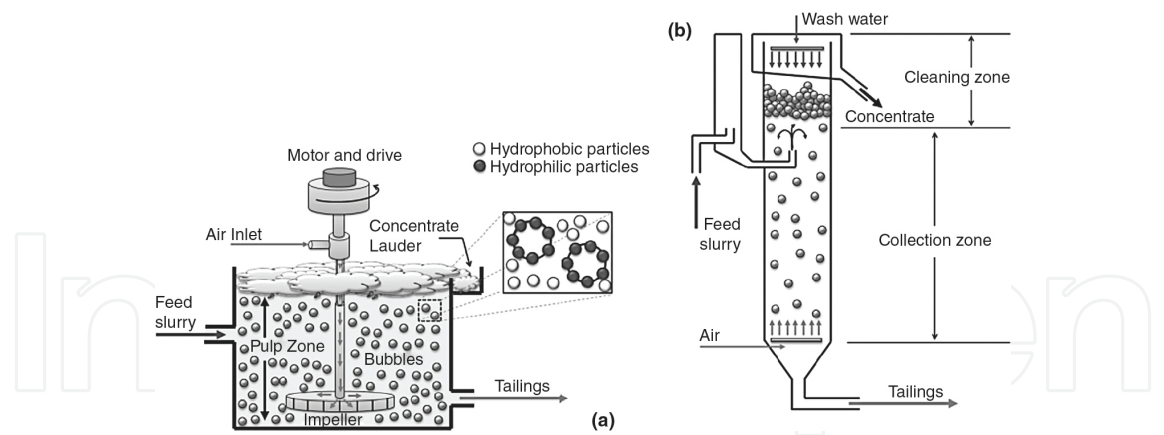


Fig. 17. Mechanical flotation cell (a) and flotation column (b) [4].

Currently, more than half of the world’s marketable phosphates are concentrated by the flotation process [46]. Two types of flotation machines are available [4]:

1. Mechanical flotation cell (**Fig. 17(a)**);
2. Colum flotation cell (**Fig. 17(b)**).

The comparison of both systems is shown in **Table 2** [4]. Phosphoric tailings are fine-grained rock produced from the flotation processes [47].

Mechanical Flotation Cells	Column Flotation
Cell sizes ranging from ~0.1 to 350 m³	Available up to 4 m in diameter
	Typical heights around 9 – 15 m
Air induced or injected through the impeller to generate bubbles	Internal or external spargers generate air bubbles
	Produces smaller bubbles
Bubble-particle interaction through mixing by impeller	Bubble-particle interaction through the countercurrent action-descending slurry and rising bubbles
Less favorable for the bubble-particle attachment	Generally considered more favorable for the bubble-particle attachment
	Better metallurgical performance (grade and recovery)
	Axial mixing can significantly reduce the overall performance (especially in larger-diameter columns)
	No moving parts
Well known to operators and easier to operate	Newer and less known by operators
Convectional plant operation history and knowledge base on mechanical cells	Harder to operate

Table 2. Comparison of mechanical flotation cell and column flotation [4].

Flotation cells are usually designed to perform several functions simultaneously, some of them are [45]:

- a. Agitation and circulation of the pulp mixture to keep all particles in suspension;
- b. Aeration, which provides further agitation, involves dissemination of fine air bubbles throughout the pulp;
- c. Promotion of particle-bubble collision facilitating selective attachment and transport. Such collisions can also be enhanced by the countercurrent flow of discrete particles and bubbles;
- d. Maintenance of quiescent pulp conditions immediately under the froth layer.

In most flotation plants, the cells are interconnected in batteries, and the first flotation stage, called roughing, permits quick rejection of most of the gangue and achieves high recoveries with low grades. A schematic circuit, which includes roughing, cleaning, re-cleaning and scavenging stages, is given in **Fig. 18**.

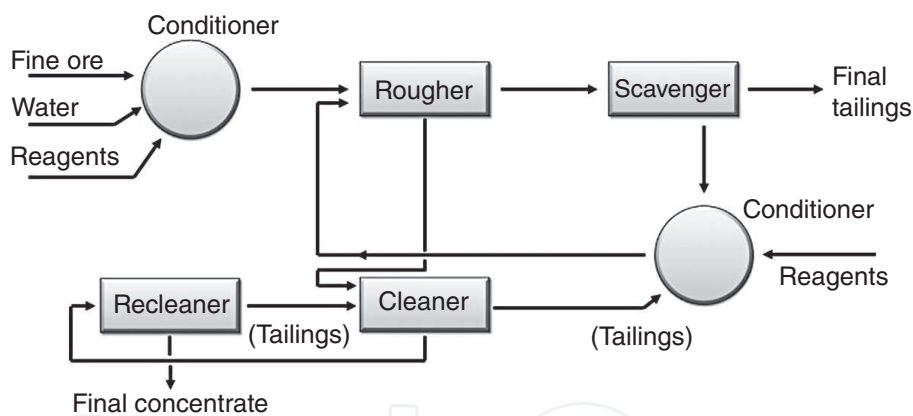


Fig. 18. Schematic representation of a flotation circuit [45]

Flotation is a dynamic process [48]. A whole range of variables can affect the performance of flotation systems (**Fig. 19**), such as their operating variables, particle size, reagents, ore composition and also the presence of ionic species in water [42],[46],[49]. The suspension of soluble minerals such as apatite is bonding large amounts of ions that interact with the mineral surface and affects the flotation performance. The interactions of dissolved anions from minerals in a pulp with a collector can form insoluble surfactant salts, which can precipitate non-selectively on mineral surface. These ions are so called potential-determining ions of fluorapatite such as Ca^{2+} , CaOH^+ , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , F^- , H^+ and OH^- [46],[50]. The effect of water quality on the flotation process was described by LIU et al [51].

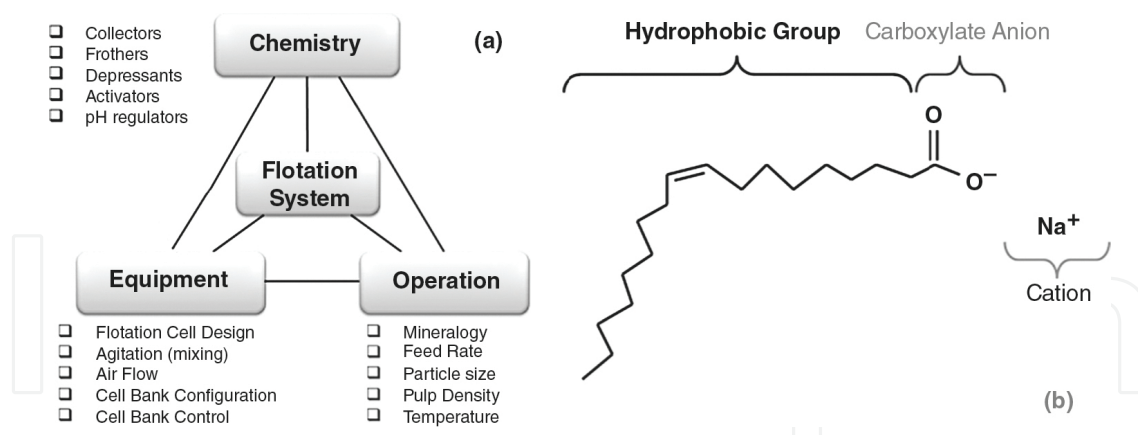


Fig. 19. Flotation system with interrelating subsystems (chemistry, equipment and operating components)(a) and sodium oleate in an anionic collector that can be used to render apatite hydrophobic in alkaline environments (b) [4].

The selectivity of froth flotation processes is highly influenced by the specificity of integrations between minerals and reagents, which are used to control the hydrophobic/hydrophilic character of mineral/water interfaces [52].

The use of additives is a tool for the control of surface tension of the flotation system. Additives (flotation reagents) used in phosphate flotation are synthetic organic species. They are produced via the ethoxylation of fatty alcohols. Alcohols are obtained from vegetable oils or animal fats. Ethylene oxide comes from the petroleum industry. These reagents may exhibit variable molecular composition and number of carbon atoms in the hydrocarbon chain, as well as the presence of double bonds, different stereochemistry (*cis-trans* isomerism) and also several levels of ethoxylation. The additives employed in phosphate ore flotation contain the carbon chains of different lengths, with a predominance of 18 carbon atoms. The ethoxylation level is represented by the average number of ethylene oxide groups in the molecule. Best results were achieved with three or four groups. The dosage of additives is 5% with respect to the collector dosage, reaching 10% under special conditions [53].

The organic reagents, such as guar gum, cashew gum, tannins, dextrin, ethyl cellulose and carboxymethylcellulose, are capable of acting as depressor in the flotation of igneous phosphate ores. The performance of corn starches was consistently superior to that of those reagents [53],[54]. The depressing ability of starch and ethyl cellulose appears to be related to steric compatibility between the positions of cations present on the mineral surface and hydroxyl groups within the molecular structure of reagents [52].

The role of surface and porosity was investigated by ZHONG et al [55]. When the samples were not aged prior to the collector (potassium oleate) addition, the floatability was controlled by the dissolution (of calcium) and adsorption (of oleate) behaviors, which, in turn, were governed by the surface area. It appears that the surface constituted by pores had lower influence on the adsorption and dissolution characteristics than the external surface. This was suggested to be due to slow diffusion of calcium through the pores, which resulted in reduced dissolution rate, as well as the non-participation of a substantial portion of pores in the adsorption process. When the samples were aged prior to the oleate addition, the bulk

precipitation of calcium oleate complex was found to play a crucial role. Since the bulk precipitation is not an interfacial process, the effect of surface area was slighter with aged samples.

A critical review of reagents used in the flotation of phosphate ores was performed by SIS and CHANDER [56]. Based on the literature, it was concluded that the usage of surfactant mixtures has certain advantages over single surfactant as the synergistic effects between surfactant mixtures were observed during different experiments such as surface tension, contact angle, adsorption and flotation. The synergism of surfactant mixtures at air/liquid, liquid/oil and liquid/solid interfaces arises from the improvement of froth properties, emulsification of hydrocarbon oil (e.g. fuel oil) and homogenous adsorption of collector on the minerals and protection of the collector from harmful effect of dissolved ions in the presence of auxiliary surfactant.

The activation of apatite particles during dry milling may enhance the adsorption of reagents, which favors the recovery of apatite. However, active defects may serve as the sites for the adsorption of water and some very fine gangue particles on the apatite surfaces, causing apatite particles to be less responsive to flotation. As a result, dry milling did not have much impact on the recovery and flotation kinetics of apatite [42].

The fact that microorganisms, both living and dead, and products derived from the organisms can function as flotation agents and flocculation agents is abundantly clear. They can modify the surfaces of minerals. They can function as flotation collectors and as flotation depressants and activators. In many cases, they or their products can function as specific flocculation agents [57].

Many strains of bacteria are able to adsorb Ca(II) and Mg(II) ions from aqueous solution and, in some cases, the adsorption can be very specific. For example, *Bacillus subtilis* typically binds Mg(II) much more readily than Ca(II). Bacteria can also adhere to the surfaces of minerals containing calcium and magnesium, either enhancing or depressing the flotation of these minerals. Since *B. subtilis* binds Mg(II) preferentially, it was reasoned that the adhesion to a mineral containing magnesium and calcium (dolomite) might be quite different from the adhesion to a mineral containing only calcium (apatite) and this difference could possibly be utilized in mineral processing. The experiments investigating the binding of Ca(II) and Mg(II) to *B. subtilis* cells were initiated, and anionic collector microflotation of pure dolomite and apatite mineral samples in the presence and absence of these bacteria was performed. Since Ca(II) and Mg(II) also bind to dolomite and apatite, the zeta-potential measurements as a function of pH in the presence and absence of these ions were performed in order to better elucidate the effect this binding may have on the attachment of *B. subtilis* to those two minerals [58].

8.8. Extraction of rare-earth elements

The group of rare earths consists of 14 lanthanides or 4f elements in the periodic table along with three more elements: lanthanum, scandium and yttrium. Lanthanides comprise 15

elements with atomic numbers 57 – 71, which include lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). All elements occur in nature, while promethium (Pm) originates as a part of radioactive decay. Elements La, Sc and Y have physiochemical properties similar to rare earths and are associated with the same minerals. Since they have similar chemical properties, the elements in the lanthanide series, yttrium and scandium, are considered as rare-earth elements (REE). Another classification used is light rare-earth elements (LREEs, atomic numbers 57 – 63: La, Ce, Nd, Pr, Pm, Sm and Eu) and heavy rare-earth elements (HREEs, atomic numbers 64 – 71: Gd, Tb, Dy, Ho, Er, Tm and Yb) [59],[60].

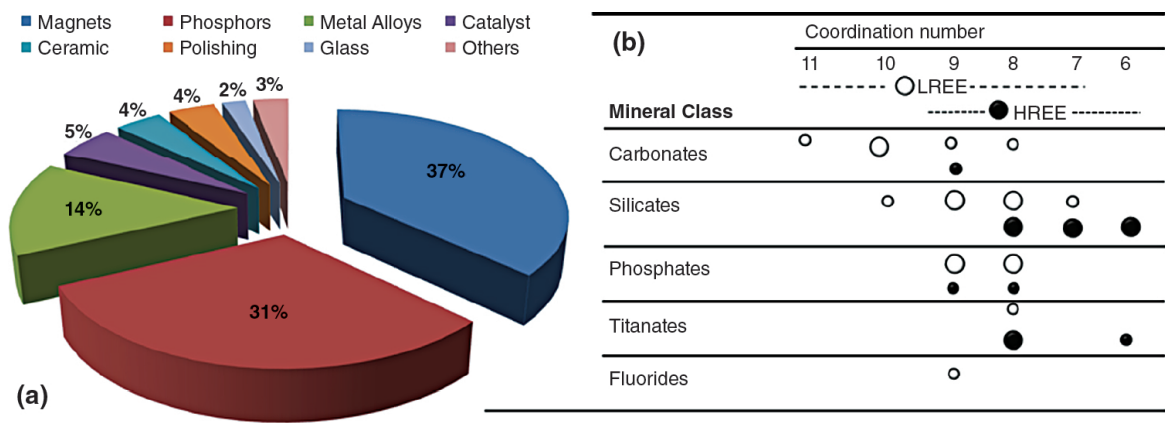
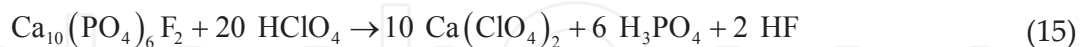
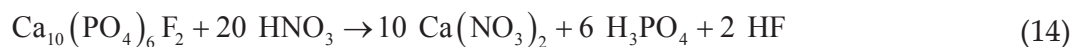


Fig. 20. Applications of REE (a) [62] and the coordination numbers and abundances of LREEs (white cycle)- and HREEs (black cycle)-bearing minerals. The size of circle indicates rough abundance of REEs for each mineral class (b) [64].

Most of the REE deposits exist in China, America, India, Middle Asian nations, South Africa, Australia and Canada. The demand for REEs has increased in recent years due to the uncertainty of the supply and high technological applications associated with their characteristic electronic, optical and magnetic properties (**Fig. 20**). RE phosphate minerals, such as monazite, florencite, xenotime, cheralite and britholite, are the most naturally abundant forms that are associated with fluorapatite [47],[61],[62],[63],[64].

The techniques described in **Chapter 8** are usually used for concentrating REE minerals prior to the extraction of REEs from phosphate rocks (PR).¹⁰ A pre-leaching stage with mineral acid (**Eq. 19** and **Eqs. 13 – 16**) can be useful in order to selectively leach the FAP fraction as well as other impurities such as sodium, potassium, magnesium, aluminum, iron, manganese, uranium and thorium associated with the FAP lattice, resulting in REE-enriched concentrate [47].

¹⁰ The processing chain for PR results in the majority of trace elements being lost either to waste disposal or to the environment (mainly soil and water) through fertilizer consumption and the food chain [47].



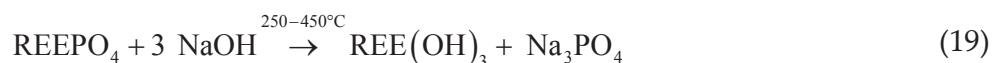
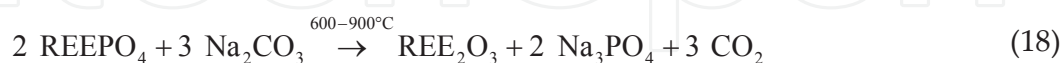
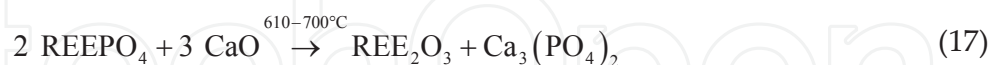
However, leaching efficiencies can vary significantly depending on the mineralogy of the ore and the type of acid used. H_3PO_4 and HF acids formed during the leaching process of FAP with acids interfere and change the leaching efficiency [61].

The effect of aliphatic and aromatic low molecular weight organic acid on the release of REEs and yttrium from phosphate minerals was investigated by GOYNE et al [65]. The performance of acid increases in the following order:

No ligand \approx salicylic acid < phthalic acid \approx oxalic acid < citric acid.

The utilization of organophosphorus reagents, such as Talcher organic phosphorus solvent (TOPS 99), an equivalent to di-2-ethylhexyl phosphoric acid, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), etc., for the extraction of REEs was also reported [66],[67],[68],[69].

Systematic study of the thermal decomposition of monazite to remove phosphate in order to achieve more complete conversion of rare-earth phosphate into its oxides was performed by KUMARI et al [62]. The method is based on roasting of monazite with CaO, Na_2CO_3 and NaOH (Fig. 21):



Washed monazite concentrate achieved from roasting was dried and leached by diluted HCl:



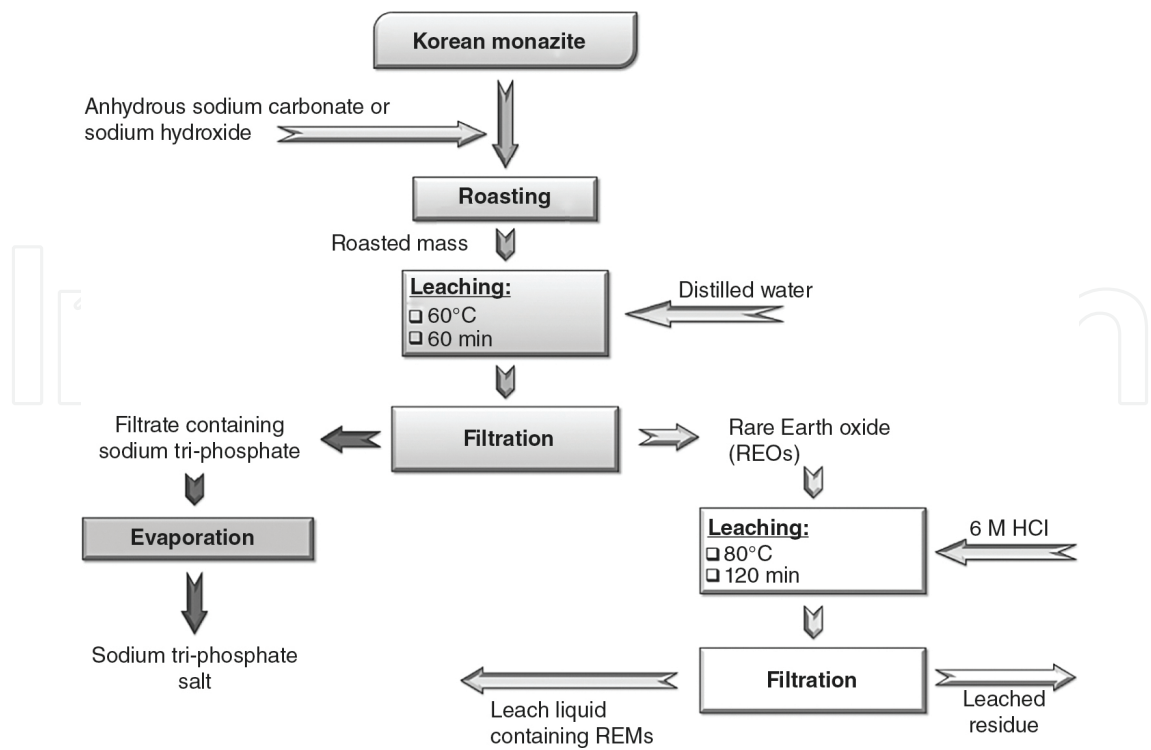


Fig. 21. Process flow sheet for the separation of phosphate and recovery of REMs from monazite [62].

Optimal condition includes 2 h of leaching by 6 M HCl at the temperature of 80°C. The pulp density should be of 30 g·dm⁻³ [62].

The optimization of leaching operation of rare-earth-bearing ores is a complex process since many attributes simultaneously affect the operation, with some of them being conflicting in nature. Therefore, a proper selection of leaching process with pertinent attributes is crucial for the user in order to maximize the percentage recovery at minimal operating costs. The methodology is proposed by BARAL et al [70]. The parameters affecting the performance of leaching operation are listed in **Table 3**.

n	Attributes of leaching process		
	Physical	Chemical	General
1	Leaching temperature	Nature of ore	Source of ore
2	Leaching time	Grade of ore	Cost of ore
3	Agitation time	Choice of leaching agent	Mode and cost of transportation of ore to the plant
4	Pressure	Acidity of leaching agent	Percentage recovery/extraction of REEs
5	Partial of mesh size of the ore sample	Corrosiveness of leaching agent	Pretreatment prior to leaching

<i>n</i>	Attributes of leaching process		
	Physical	Chemical	General
6	Liquid-to-solid ratio	Reducing agents along with leaching agent	Cost of leaching agent
7	Size of the leaching tank	Percentage gangue/impurities in ore	Cost involved in pretreatment of ore
8	Amount of ore to be processed	Roasting of ore before leaching	Cost involved in mechanical agitation
9	Amount of leaching agent to be handled	Dissolution rate of REEs	
10	Number of leaching stages	Solubility of other elements along with REEs	

Table 3. Operating conditions affecting the performance of leaching procedure [70].

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